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(54) A CONTROLLING AGENT FOR, AND A METHOD OF, CONTROLLING INJURIOUS INSECTS

(71) We, MATSUSHITA ELECTRIC WORKS LTD., of No. 1048 Oaza Kadoma, Kadoma-shi, Osaka, Japan and SUMITOMO CHEMICAL COMPANY LIMITED, of No. 15 Kitahama 5-chome, Higashi-ku, Osaka-shi, Osaka, Japan, both Japanese Companies, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a controlling agent for controlling injurious insects, to a method for producing such a controlling agent, and also to a method for effectively dispersing the active ingredients present in the controlling agent to thereby control injurious insects.

Injurious insects are notoriously hazardous and unsanitary, and many methods for controlling them have heretofore been suggested. It is known in the art, for example, as disclosed in Japanese Patent Application (OPI) No. 44415/73 to use a pyrethroid compound in order to control injurious insects. Further, Japanese Patent Application (OPI) No. 64426/75, for example, discloses that an active ingredient for controlling injurious insects can be carried in rising heated air. None of such methods, however, work well unless these exterminating agents and methods of employing such result in the agent coming into contact with the insects.

Further, heating of a mat impregnated with the active ingredient to thereby vaporize the active ingredient contained therein has been proposed. In accordance with this method, the active ingredient slowly vaporizes from the surface of the mat and thus, a large amount of the active ingredient cannot be dispersed in a closed space within a short period of time. Accordingly, this method generally is exclusively used for controlling mosquitoes and is not sufficient for controlling cockroaches and other injurious insects.

In addition, a method of incinerating the controlling agent *per se* has also been hitherto proposed as a prior art method of controlling injurious insects. In accordance with this method, a large amount of the active ingredient present in the controlling agent can be supplied even in small confined spaces within buildings and thus, the defects of the above-described prior methods can be reduced. However, since in this method the active ingredient comes into contact with bodies of the injurious insects in a condition where the active ingredient is adhered to particles of combustion products having a large particle size, sufficient contact of the active ingredient with the insects is not obtained and the controlling effect which can be achieved is low. Also, there is the possibility that due to the generation of smoke during incineration smoke sensors provided in the buildings are activated or it can be mistakenly assumed that a fire is occurring.

An object of this invention is therefore to minimise or alleviate the above-mentioned disadvantages referred to in the prior art.

In one aspect, the invention resides in a controlling agent for controlling injurious insects which comprises, as an active ingredient, an insecticidally effective amount of at least one insecticidal compound retained in a porous solid mineral material, the controlling agent having a ratio of the total surface area to the volume of 5:1 cm^{-1} or higher.

In a further aspect the invention resides in a method for producing the

controlling agent described above by impregnating a molded porous mineral material with at least one insecticidally active compound, or mixing and kneading a powder of a mineral material with at least one insecticidally active compound and then molding the resulting mixture.

In yet a further aspect the invention resides in a method for controlling injurious insects which comprises heating the controlling agent utilizing a rising heated air current capable of heating the controlling agent at 200 to 430°C to thereby vaporize the active ingredient in the controlling agent within a short period of time and causing the vaporized active ingredient to come into contact with injurious insects.

In the accompanying drawings:—

Figure 1 illustrates the test conditions used in Example 4 hereinafter described, and shows the arrangement of an electrically heated fumigator 1 and Petri dishes containing test cockroaches 2, 3, 4, 5 and 6 in an experimental chamber.

Figure 2 illustrates the test conditions used in Example 7 hereinafter described, and shows the arrangement of an electrically heated fumigator 1 and Petri dishes containing test cockroaches 2, 3, 4, 5, 6, 7, 8 and 9 in an experimental chamber.

Figure 3 is a perspective view of a device for heating the controlling agent of this invention,

Figure 4 is a perspective view of the heating element used in the heating device of Figure 3,

Figure 5 is a perspective view of one embodiment of the controlling agent of this invention, suitable for use in the heating device of Figure 3.

In order to supply an insecticidally effective amount of one or more insecticidal compounds in a rising hot air current in a short period of time, without using any other carrying medium for diffusion of the active ingredients, the present invention provides a controlling agent comprising a porous solid mineral material containing at least one insecticidal compound as an active ingredient (the term "porous" is used herein to describe, a "perforated", "sieve-like" or "granular" material or form). By use of the controlling agent of the present invention, it becomes possible to control insects, that is crawling insects such as cockroaches, and flying insects such as flies, and mosquitoes, etc., which are harmful, unsanitary and uncomfortable.

The controlling agent of the present invention is also useful for controlling insects harmful to stored cereals, agricultural crops and household horticultural plants.

The controlling agent of the present invention is prepared by kneading one or more suitable insecticidally active compounds as an active ingredient together with a suitable porous solid mineral material (referred to as a "carrier" hereinafter), followed by molding, or impregnating a previously molded carrier with one or more insecticidally active compounds. When the thus prepared controlling agent is heated by a suitable heat source, the active ingredient present in the controlling agent is vaporized and efficiently diffused into a space by a rising hot air current through pores in the carrier. In this way, the controlling agent of the present invention is used to provide the active ingredient thereof in a diffused state.

According to the method of the present invention the active ingredient in the controlling agent is vaporized and the active ingredient vapor flows into small gaps or spaces in a short time even though it is not diluted in the controlling agent. It is thus possible to control various kinds of harmful insects cleanly, simply, without labor and in a short time without pollution of application sites by components other than the active ingredient.

It is known in the art to use electric mosquito fumigators for controlling mosquitoes. However, with this prior art approach, it is not possible to achieve a harmful insect controlling effect in a short period of time.

The method for applying the controlling agent containing at least one insecticidal compound as an active ingredient to injurious insects is described below. Since a problem exists specifically with respect to control of cockroaches, the description given herein will be directed particularly to cockroaches as a representative example of injurious insects against which this invention is effective. A first requirement of the method is to convert the above active ingredient into fumes under certain specified conditions and thereby to disperse the active ingredient as fumes in a closed space. The active ingredient can be vaporized by heating. A second requirement of the method is that the active ingredient should be

supplied in a small amount yet at a high concentration into a closed space within short periods of time. To meet these requirements, it is necessary to determine how the active ingredient is selected, how to formulate the active ingredient into preparation forms suitable for heating fumigation, how the active ingredient is supplied to a means for fumigation under heating, the conditions for heating, the concentration of the active ingredient in the ambient atmosphere, the time required to achieve this concentration, and the time for which the predetermined active ingredient concentration is to be maintained.

The concentration of the fumes of the active ingredient is not particularly limited, but preferably, the concentration is 5 to 100 mg/m³ preferably 15 to 50 mg/m³.

The active ingredient in such high concentrations enters small spaces inhabited by cockroaches and comes into contact with the cockroaches. The active ingredient in high-concentration adheres to or is absorbed by the bodies of the cockroaches, whereby the cockroaches are flushed out from their normal habitat or dark places to a wide open space in the room. For a certain period of time, the cockroaches wander about, and in about 20 to 60 minutes, they collapse. Once the active ingredient in the predetermined concentration had adhered to or has been absorbed by the bodies of the cockroaches, they are killed almost without fail.

The active ingredient in accordance with this invention is applied in as high a concentration as possible to reduce the amount of the active ingredient used, and the active ingredient is supplied within a short period of time to maintain the active ingredient in the atmosphere at a predetermined concentration. For this purpose, the rate of release of the active ingredient in the form of fumes, or the time required until the predetermined concentration of the active ingredient is reached, should be within a certain specified range. Generally, it is 5 to 100 mg/m³/10 minutes, preferably 15 to 50 mg/m³/10 minutes.

Vaporization of the active ingredient in a predetermined concentration should be effected reasonably rapidly. In particular, the time required to effect vaporization of the active ingredient in a predetermined concentration should be of the same order as the periods of time which are preferred in terms of controlling efficiency and controlling effect. Usually, the predetermined concentration preferably is achieved within 3 to 30 minutes from the beginning of the fumigation. More preferably, the conditions are set such that the predetermined concentration is reached within 5 minutes.

For the above purpose, various conditions for fumigation are prescribed. For example, the fumigating temperature is generally 200 to 430°C, preferably 250 to 400°C.

If the temperature is below about 200°C, achieving a predetermined concentration of the active ingredient in the atmosphere is too time-consuming, and a settling of the fumes begins. If the temperature exceeds about 430°C, the active ingredient decomposes at an increasing rate. The temperature range may vary depending on the type of active ingredient used.

By considering the required conditions set forth above, the amount of the active ingredient in the controlling agent is determined.

The shape of the fumigator may have any of a circular, square or other cross-sectional form and a preferred fumigator is a heat-resistant, tube-like vessel. The controlling agent is placed at the upper portion of the tube-like vessel and a heat source is placed at the lower portion thereof. Furthermore, the fumigator is preferably such that a predetermined temperature is reached within 10 minutes and that temperature is maintained for a predetermined period of time, and is constructed so that the active ingredient in the controlling agent can be vaporized and diffused in a rising hot air current in a short time.

In preparing the controlling agents containing the active ingredient of the invention, the following conditions are exemplary, in view of the various conditions, to enable efficient vaporization of the active ingredient.

(1) As described above, the controling agent of this invention contains a carrier and the desirable properties for the carrier used in admixture with the active ingredient are as follows:

(a) The carrier should have the ability to hold the active ingredient well. Whether by a capillary phenomenon or by physically weak adsorption, the carrier should preferably hold the active ingredient in the controlling agent, and be considered dry under normal conditions when touched with a finger.

(b) The carrier should not degrade the active ingredient.

(c) The active ingredient should be capable of being vaporized efficiently from

the carrier. In other words, the active ingredient should not remain adsorbed on the carrier but should be released from the controlling agent once the controlling agent has been heated. The active ingredient does not need to be released at once from the carrier and it is sufficient if the active ingredient is released within an appropriate period of time.

(d) The carrier should have some degree of heat stability, and preferably some degree of fire retardancy, because burning of the carrier during release of the active ingredient is dangerous.

(e) The carrier, preferably, should be moldable, since molding of the controlling agent into a definite form is preferred for use.

(f) The carrier should preferably have good thermal conductivity.

Examples of suitable carriers that can be used in the controlling agent are cement, gypsum ($CaSO_4$), silica, diatomaceous earth, alumina, perlite, calcium silicate, titanium oxide, calcium carbonate and barium sulfate. A binder or a reinforcing agent, (e.g., glass fibers, asbestos or cellulose) can be used along with the carriers, if desired.

(2) The controlling agent comprises at least one insecticidally active compound as an active ingredient in admixture with a specific type of carrier and other conventional additives (such as a binder facilitating the molding of the controlling agent, an agent for improving thermal conductivity, and agents for increasing the action of the active ingredient). The amount of the active ingredient is usually 3 to 30% by weight. If the amount of the active ingredient is below about 3% by weight, the time required for migration of the active ingredient in the controlling agent becomes long. Thus, either the release of the active ingredient is time consuming, or the release is not completed within the predetermined period, with the controlling agent retaining a considerably large amount of the active ingredient. Furthermore, the controlling agent becomes bulky. On the other hand, if the amount of the active ingredient exceeds about 30% by weight, the active ingredient exudes out of the controlling agent and is lost. For example, the active ingredient adheres to the hands or devices during handling. Alternatively, the active ingredient may adhere to the equipment used during production of the controlling agent. Furthermore, the active ingredient may degrade in the working environment during manufacture and other processing, thereby resulting in, for example, emission of an offensive odor. Further, the ability to mold the controlling agent is decreased at the time the controlling agent is formed into its final form. Moreover, when the controlling agent is vaporized, the active ingredient flows out and boils due to the effect of heat, and is scattered thereby increasing the loss of the active ingredient.

The controlling agents of the present invention should be formulated, so that the active ingredient present therein can be easily used for fumigating and released on heating. Specifically, the controlling agent should be porous, and when it is placed on a fumigator it is preferred for the contact area between the controlling agent and an air current around the controlling agent to be as large as possible. Consequently, a preferred form of the controlling agent is a porous plate form, a porous cylindrical form or a sieve-like form. Also, even granular forms can be used by placing the granules in a suitable vessel or by molding, as long as the particle size is not too small. The ratio of the surface area to volume of the carrier is 5:1 cm^{-1} or higher.

Any compound which is sufficiently insecticidally active to control harmful insects and satisfy the foregoing requirements may be used as the active ingredient. Suitable insecticidally active compounds which can be used in this invention as the active ingredient include pyrethroid type compounds, carbamate type compounds and phosphorous type compounds.

Examples of suitable pyrethroid compounds which can be used as an active ingredient in the controlling agent of this invention are pyrethrins, allethrin [(±)2 - allyl - 3 - methyl - cyclopent - 2 - en - 1 - one - 4 - yl - chrysanthemate and the isomers thereof arising from differing positioning of the alcohol or acid moiety], Tetramethrin [N - (3,4,5,6 - tetrahydrophthalimide) - methyl(±) - cis,trans - chrysanthemate and the isomers thereof arising from differing positioning of the acid moiety], resmethrin [5 - benzyl - 3 - methylfuryl(±) - cis,trans - chrysanthemate and the isomers thereof arising from different positioning of the acid moiety], furamethrin [5 - propargylfurfuryl - chrysanthemate and its isomers], phenothrin [3 - phenoxybenzylchrysanthemate and its isomers], permethrin [3 - phenoxybenzyl(±) - cis,trans - 3 - (2,2 - dichlorovinyl) - 2,2 - dimethyl - 1 - cyclopropane carboxylate and its isomers], cypermethrin [(±)α - cyano - 3 -

phenoxybenzyl(±) - cis,trans - 3 - (2,2 - dichlorovinyl) - 2,2 - dimethyl - 1 - cyclopropane carboxylate and its isomers], phenvalerate [(±)α - cyano - 3 - phenoxybenzyl - 2 - (4 - chlorophenyl) - isovalerate and its isomers], decamethrin [(−)α - cyano - 3 - phenoxybenzyl(+) - cis - 3 - (2,2 - dichlorovinyl) - 2,2 - dimethyl - 1 - cyclopropane carboxylate and its isomers], kadethrine [a tradename of Roussel-Uclaf for 5 - benzyl - 3 - furylmethyl(+) - cis - 2,2 - dimethyl - 3 - (2,3,4,5 - tetrahydro - 2 - oxothien - 3 - ylidenemethyl) - cyclopropane carboxylate and its isomers].

Examples of the carbamate compounds which can be used as the active ingredients include propoxer, methyl 3,4-xylylcarbamate, methyl m-cresylcarbamate, methyl o-secbutylphenylcarbamate and carbaryl. Examples of the organophosphorous compounds which can be used as the active ingredient include diazinon, DDVP, fenthion, fenitrothion, Dursban (registered Trade Mark), and actellic.

Since the present invention is characterised by dispersing the active ingredient in the form of fumes in the air, injurious insects and cockroaches in particular can be controlled easily and effectively.

As described above, the controlling agent of this invention is used by heating. A suitable heating means for heating the controlling agent of this invention is described in detail in the following.

Organic insecticidally active compounds are unstable to heat and previously it has been thought that it is desirable to vaporize organic insecticidally active compounds at temperatures which are not very high. For example, using conventional electric mosquito fumigators, 4 to 8 hours are required to vaporize 30 to 80 mg of an organic insecticidally active compound.

In the present invention, an apparatus described hereinbelow is devised to execute a rapid vaporization of the active ingredient using a heated air current. That is, a heating means is provided at a lower position inside a cylindrical container where the height of the cylindrical container is equal to or larger than the diameter of the cylindrical container, and a controlling agent is placed above the heating means. Using this construction, air is heated to form a rising air current. This rising air current comes into contact with the controlling agent, heats the same, vaporizes the active ingredient therein, and causes fumes of the active ingredient to be passed out and dispersed all over a closed space.

A preferred embodiment of a heating apparatus for the controlling agent of the present invention is described in detail with reference to Figures 3 to 5. In figure 3, numeral 11 indicates a container, 10 indicates a heating means, and 16 indicates legs which support the container 11. Container 11 is an open-ended cylindrical container and the height of cylindrical container 11 is preferably the same as or longer than the diameter of the cylinder. For example, the height is 10 cm and the diameter is 7.2 cm. This is required to obtain a so-called chimney effect. That is, air heated by heating means 10 positioned at a lower position in cylindrical container 11 rises as a hot air current and heats a controlling agent 19 positioned at a higher position in cylindrical container 11.

Accordingly, a lower opening 11b of cylindrical container 11 preferably is as large as possible. However, lower opening 11b is not necessarily provided at the bottom 11c of container 11, and the opening may be provided at the lower portion of the side of container 11. In any case, heating means 10 should be positioned above the opening for taking in air.

A supporting means which supports controlling agent 19 is provided at a higher position than heating means 10. Since controlling agent 19 must be supported yet be capable of being removed, the supporting means of controlling agent 19 is specifically constructed as a controlling agent seating portion 17. The seating portion 17 may be made of wire mesh or a wire lattice, and furthermore it may be defined by projections (not shown) which extend from the inside of container 11 to support the solid controlling agent 19. In short, the seating portion 17 should be made so that passage of a heated air current is permitted efficiently. In addition, the portion 17 is preferably arranged so that controlling agent 19 does not extend above the top 11a of cylindrical container 11. The purpose of this construction is to inhibit air currents in a transverse direction and to blow the vaporized fumes of the active ingredient as high as possible toward the ceiling of the space being fumigated.

As shown in Figure 4, the heating means 10 can be an electric heater, and is constructed by surrounding the heater elements 12 with an enclosure 13. The

heating means 10 is connected by a power supply cord 14 to a plug for connection to a power supply.

Legs 16 support cylindrical container 11 at a position off of the floor, for example, 5 cm above the floor, so as to permit air to be taken in from the bottom of container 11. Accordingly, when openings for taking in air are provided at a lower portion of the side of the container 11, legs 16 need not be employed provided the container 11 is thermally and electrically insulated from the floor.

In the present invention, the heating means should have a large capacity to rapidly generate a heated air current of about 200 to 430°C. Furthermore, the controlling agent is porous so that the active ingredient previously impregnated into the controlling agent as described above is released rapidly.

Also, as shown in Figure 5, pores 19*a* of the controlling agent preferably are those through which a rising aircurrent can easily pass, that is, vertical pores 19*a* which are provided in the same direction as that of the rising air current.

By using the heating apparatus described above, it is possible to rapidly generate a heated air current to heat the porous solid controlling agent and to rapidly vaporize the active ingredient impregnated in the controlling agent without decomposition of the active ingredient. Thus, using this approach it is possible to attain a desirable injurious insect controlling effect.

The following Reference Examples and Examples are given to illustrate the present invention in greater detail.

Reference Example 1

A pyrethroid compound was incorporated into each of the plates of solid porous mineral materials shown in Table 1 below, and the plates were heated for 20 minutes with a rising current of hot air at 320°C to vaporize the pyrethroid compound contained therein. In this manner, it was noted that the percent release of the pyrethroid compound varied depending upon the type of mineral material of the plate. The plate used in this reference example was prepared by molding the indicated mineral material using a die having the same size.

TABLE 1

Mineral Material	Weight of Mineral Material (g)	Weight of Pyrethroid Compound (g)	Amount of Compound Remaining After Vaporization (g)	Percent Release of Compound (%)
Gypsum ($CaSO_4$)	4.68	0.78	0.08	89.8
Alumina Cement	5.87	0.78	0.05	93.8
Unglazed Pottery	9.44	0.81	0.33	59.5
Mixture of Portland Cement and Asbestos	4.87	0.72	0.10	82.3
$CaSiO_3$	5.67	1.20	0.08	93.4
SiO_2	4.97	1.24	0.08	93.5
Al_2O_3	8.99	1.21	0.07	94.5
$CaCO_3$	4.30	1.19	0.15	87.4
$BaSO_4$	6.64	1.59	0.09	94.3
TiO_2	5.31	1.15	0.12	98.6

The above measurements were conducted using the following procedure. The mineral material plate was first weighed and a solution of permethrin in a solvent was then poured into the material. The plate was then dried for 24 hours to remove the solvent and the plate was again weighed to determine the weight of the compound absorbed. After vaporization of the pyrethroid compound by heating, the plate was weighed again to determine the weight of the compound remaining in the plate after vaporization and also the amount of the pyrethroid compound released. The temperature of the rising air current was determined at the bottom of the mineral material plate.

The same procedure as in the above was performed using a porous cylindrical solid controlling agent (thickness: 3 mm; outside diameter: 50 mm; numerous pores with a diameter of 2 mm penetrating in the thickness direction), a porous rectangular sheet-like solid controlling agent, and a 3 mm thick gypsum board impregnated with an active controlling ingredient and sandwiched between two porous slate boards. Similar results were obtained.

Reference Example 2

In this reference example, the relationship between the temperature of the rising current of air and the percent effective vaporization of the active ingredient and the relationship between the time and the percent effective vaporization of the active ingredient were determined using permethrin as the active ingredient.

99% alumina as a solid porous mineral material was first molded into a disc having a diameter of 47 mm, a height of 12.5 mm, a pore diameter of 3 mm (in the height direction) and 102 pores and the molded plate was then sintered. Permethrin was dissolved in a solvent and the solution was absorbed in the disc to produce a solid controlling agent. The solid controlling agent thus obtained was dried at room temperature for 24 hours and then tested. The amount of the active ingredient was 10% by weight (dry basis) based on the total weight of the resulting solid controlling agent.

The solid controlling agent was placed in a fumigator, in which the temperature of the current of rising air could be freely controlled, whereby the permethrin was vaporized by the ascending hot current air. The thus vaporized permethrin was captured by adsorption on silica gel and an acetone solvent, and then gas chromatographed to measure the percent effective vaporization of permethrin initially used.

(1) The relationship between the vaporization temperature and the percent effective vaporization of permethrin is shown in Table 2 below. In this regard, the temperature of the rising hot air current was changed within the range of from 200° to 430°C whereas the time of passage of electric current to the vaporizer was set at 20 minutes.

TABLE 2

Temperature of Rising Hot Air Current (°C)	Amount of Alumina (g)	Initial Amount of Permethrin (g)	Amount of Permethrin Detected (g)	Percent Vaporization of Permethrin (%
200	18.00	2.00	1.20	60.0
260	18.00	2.00	1.68	84.0
280	18.00	2.00	1.77	88.5
300	18.00	2.00	1.74	87.0
320	18.00	2.00	1.76	88.0
340	18.00	2.00	1.74	87.0
360	18.00	2.00	1.73	86.5
380	18.00	2.00	1.72	86.0
400	18.00	2.00	1.72	86.0
430	18.00	2.00	1.60	80.0

(2) The relationship of the time of passage of the electric current to the vaporizer and the percent effective vaporization of permethrin is shown in Table 3 below. In this regard, the time of passage of the electric current was changed within the range of from 3 to 30 minutes, whereas the temperature of the rising hot air current was set at 320°C.

TABLE 3

Time of Passage of Electric Current (min)	Amount of Alumina (g)	Initial Amount of Permethrin (g)	Amount of Permethrin Detected (g)	Percent Vaporization of Permethrin (%)
3	18.00	2.00	0.95	47.5
5	18.00	2.00	1.39	69.5
7	18.00	2.00	1.76	88.0
10	18.00	2.00	1.76	88.0
15	18.00	2.00	1.74	87.0
20	18.00	2.00	1.73	86.5
30	18.00	2.00	1.75	87.5

The foregoing results demonstrate that the conditions of a temperature ranging from 200° to 430°C, preferably 260° to 400°C, with a time of passage of an electric current of 5 minutes or longer impart the desired effect.

Reference Example 3

Using permethrin as the pyrethroid compound, the relationship of the percent effective vaporization to the shape of the porous solid mineral material was evaluated. A temperature of the rising hot air current of 320°C and a time of passage of the electric current of 10 minutes were employed as the vaporization conditions. Alumina was employed as the mineral material, and the same method for adsorbing permethrin into the mineral material as was used in Reference Example 2 above was employed.

(1) The size of the mineral material was such that the diameter was 33.4 mm, the height was 13 mm and the number of pores was 16, whereas the pore diameter was varied from 1 mm to 5 mm. The relationship between the pore diameter and the percent effective vaporization of permethrin is shown in Table 4 below.

TABLE 4

Pore Diameter (mm)	Initial Amount of Permethrin (g)	Amount of Permethrin Detected (g)	Percent Effective Vaporization of Permethrin (%)	K-Value* (cm^{-1})
1	1.20	0.58	48.3	3.3
2	1.20	0.71	59.1	4.0
3	1.20	0.75	62.5	4.8
4	1.20	0.79	65.8	6.0
5	1.20	0.84	70.0	8.0

*K-Value=(Total surface area)/(Volume)

It can be seen from the foregoing results that when the pore height and the number of pores are kept constant, a large pore diameter gives rise to better results than a smaller pore diameter.

(2) The size of the mineral material was such that the diameter was 33.4 mm, the height was 13 mm and the pore diameter was 3 mm, whereas the number of pores was varied as shown in Table 5 below. The relationship between the number of pores and the percent effective vaporization of permethrin is shown in Table 5 below.

TABLE 5

Number of Pores	Initial Amount of Permethrin (g)	Amount of Permethrin Detected (g)	Percent Effective Vaporization of Permethrin (%)	K-Value (cm^{-1})
8	1.20	0.60	50.0	2.1
16	1.20	0.75	62.5	4.8
32	1.20	0.88	73.3	7.8
48	1.20	1.05	87.7	12.0

It can be seen from the above-described results that when the height and pore diameter are kept constant, a larger number of pores gives rise to better results than a smaller number of pores.

(3) The size of the mineral material was such that the diameter was 33.4 mm, the pore diameter was 3 mm and the number of pores was 4.8, whereas the height of the pores was varied as shown in Table 6 below. The relationship between the height of the pores and the percent effective vaporization of permethrin is set forth in Table 6 below.

TABLE 6

Height (mm)	Initial Amount of Permethrin (g)	Amount of Permethrin Detected (g)	Percent Effective Vaporization of Permethrin (%)	K-Value (cm^{-1})
8	1.20	1.09	90.8	12.9
10	1.20	1.06	88.3	12.4
13	1.20	1.05	87.7	12.0
16	1.20	0.90	75.0	11.6
20	1.20	0.80	66.0	11.3

It can be seen from the foregoing results that when the pore diameter and number of pores are kept constant, a lower pore height gives rise to better results than a higher pore height.

In view of the foregoing, it is preferred from the stand point of the percent effective vaporization of permethrin for the surface area of the pore through which the rising air current passes to be as large as possible, i.e., for the K-value to be as high as possible. Further, it is also preferred for the height of the pores to be controlled to be as low as possible and the height of the pores is preferably less than 50 mm, preferably less than 20 mm.

Reference Example 4

The flow rate of the rising air current generated by various types of electrically heated fumigators was determined at an ambient temperature of 17°C, and the results obtained are as follows.

(1) In a fumigator of the type where a heater at 600°C was mounted inside and at the middle of an open-ended hollow cylindrical container having a diameter of 7.2 cm and a height of 10 cm and placed 5 cm above the floor, the flow rate of the heated air current at a height of 40 cm from the floor was found to be 0.5 m/sec.

(2) In a fumigator of the type where a heater at 600°C was mounted inside and at the bottom of a cylindrical container having a diameter of 7.2 cm and a height of 25 cm. The container open at the upper end thereof and was placed on the floor, the flow rate of the heated air current at heights of 40 cm and 30 cm from the floor was found to be 0.1 m/sec and 0.2 m/sec respectively.

(3) In a type of fumigator where a flat plate heater at 600°C was mounted at a height of 1 cm from the floor, the flow rate of the heated air current at a height of 5 cm from the floor was found to be less than 0.1 m/sec.

Example 1

A slate board was produced from alumina cement and asbestos. Circular plates with a thickness of 5 mm and a diameter of 35 mm were cut out from the slate board. Circular pores with a diameter of 2 mm were provided in each of the circular plates. The circular plate was heated to 70°C. A pyrethroid compound was heated to 70°C, and each heated circular plate was immersed in the pyrethroid compound to prepare a controlling agent having an active ingredient concentration of 15% by weight.

Cockroaches were controlled by using the resulting controlling agent. The places of application were areas where cockroaches were known to be present such as in restaurants of varying size.

When the heating temperature of the carrier was 50 to 70°C, the carrier seemed to be convenient for impregnation of the active ingredient (pyrethroid compound).

The results obtained are tabulated in Table 7 below.

TABLE 7

Concentration in the Atmosphere (mg/m³)	5	15	20	30	50	100	20	30
Area of the Room (m²)	9	12	16	12	20	9	16	12
Heating Temperature (°C) for the Controlling Agent	380	430	350	360	280	250	200	250
Time during which the Room was Closed (minutes)	180	180	180	150	180	150	180	180
Time Required to Attain the Predetermined Concentration in the Atmosphere (minutes)	10	10	10	10	10	10	10	10
Species of Cockroaches	G	G	B	B	G	B	B	G
Number of Cockroaches Killed	63	230	520	18	1200	314	53	88
Active Controlling Ingredient (pyrethroid)	A	A	A	A	A	A	B	C

Note

(*) G=German cockroach (*Blattella germanica*)
B=Brown cockroach (*Periplaneta picea* Shiraki)

(**) A: permethrin, B: Tetramethrin, C: d-Phenothrin

Further, the controlling effect for cockroaches was evaluated over a 2 month period of time by arranging a paper to which a tackifier was applied at areas where cockroaches were known to be present at a rate of one piece per 3 m^2. As a result, no cockroaches at all were found except four cockroaches were caught at areas where the concentration of permethrin in the atmosphere was 5 mg/m^3.

Example 2

Highly pure alumina was employed as a porous plate-liked solid in this example. The alumina was molded into a molded article with a diameter of 47 mm, a height of 12.5 mm, a pore diameter of 3 mm and a number of pores of 102, and the molded article was then sintered at 1600°C. 2 g of permethrin dissolved in a solvent was poured into the thus sintered alumina article and the mass was then dried to obtain a solid controlling agent with a permethrin content of 10% by weight based on the total weight of the solid controlling agent. The thus obtained solid controlling agent was vaporized in a kitchen with a volume of 40 m^3 in a reinforced ferroconcrete house by adjusting the temperature of the rising hot air generated from a fumigator at 300°C while passing an electric current through the fumigator for 15 minutes, and the kitchen was kept closed for 150 minutes. As the result, it was found that 239 adult cockroaches and 75 cockroach larvae were flushed out and killed.

Further, when the controlling effect was examined over a 3 month period of time in the same manner as that described in Example 1, no cockroaches at all were found.

Example 3

Highly pure silica was employed as a porous plate-like solid in this example. The silica was molded into a molded article with a diameter of 33.4 mm, a height of 13 mm, a pore diameter of 3 mm and a number of pores of 48, and the molded article was then sintered at 1000°C. 0.8 g of Tetramethrin and 0.4 g of d-Phenothrin were poured in the thus-obtained silica article in the same manner as that described in Example 2 to obtain a solid controlling agent.

The thus obtained solid controlling agent was vaporized in a kitchen with a volume of 16 m^3 in a wooden house by adjusting the temperature of rising heated air generated from a fumigator at 260°C while passing an electric current through the fumigator for 20 minutes, and the kitchen was kept closed for 180 minutes. As a result, it was found that 93 adult German cockroaches and 29 German cockroach larvae were flushed out, knocked down and in a syncopic state. However, 24 hours later none of the cockroaches were alive.

Thereafter, when the controlling effect was examined over a one month period of time in the same manner as that described in Example 1, no cockroaches at all were found.

Example 4

The sintered material prepared as described in Reference Example 2 was immersed in an ethyl acetate solution of permethrin at predetermined various concentrations which, upon fumigation, release permethrin at the concentration indication in Table 8 below, followed by air-drying to obtain a solid controlling agent containing a permethrin.

An electrically heated fumigator and 5 Petri dishes (14 cm diameter×7 cm height) each containing 10 German cockroaches (*Blattella germanica*) were arranged on the floor of an experimental chamber of a volume of 2.8 m^3 (2.65 m width×4.3 m depth×2.54 m height) as shown in Figure 1. More specifically, 3 Petri dishes each containing 10 cockroaches (2, 3 and 4) and 2 Petri dishes each containing a triangular shelter (3 cm one side×15 cm height) of plywood board at the center of the dish and containing 10 cockroaches in the shelter (5 and 6) were arranged at the distance shown in Figure 2. The electrically heated fumigator (1) was arranged in the center of the floor of the experimental chamber.

The above prepared permethrin-containing solid controlling agent was then heated on the fumigator for 15 minutes and the number of cockroaches which were flushed out from the triangular shelter to the Petri dishes 5 and 6 and the number of cockroaches knocked down in the Petri dishes 2, 3 and 4 were observed with the lapse of time. 90 minutes after the initiation of fumigation, the chamber was evacuated and each group of the cockroaches tested were collected in a glass container for observation and allowed to stand for 72 hours with feeding. The number of the cockroaches knocked down was counted 24 hours after the

fumigation and the number of the cockroaches killed was counted 72 hours after the fumigation. The results obtained are shown in Table 4 below.

TABLE 8

Effects on Cockroaches by Fumigation of Permethrin at Various Concentration

Test Conditions	Observation	Biological Effects at Various Fumigation Concentrations (mg/m³) 5	10	20	40	100
Triangular Shelter (Petri dishes 5 and 6)	FT 50* (min)	28.4	18.8	12.8	12.0	11.0
	Knocked Down (%) After 24 Hours	80	90	100	100	100
	Mortality (%) After 72 Hours	70	80	100	100	100
	KT 50** (min)	37.0	26.5	17.0	14.6	12.5
Petri Dishes (2, 3 & 4)						
	Knocked Down (%) After 24 Hours	77	87	100	100	100
	Mortality (%) After 72 Hours	70	83	100	100	100

*FT50: Time required for 50% flushing out (min)
**KT 50: Time required for 50% knock down (min)

Example 5

The sintered material prepared as described in Reference Example 2 was immersed in an acetone solution of each of the active ingredients shown in Table 9 below at a predetermined concentration which, upon fumigation, would release the active ingredient at a concentration of 40 mg/m³ followed by air-drying to obtain a solid controlling agent in each instance.

A cage having a diameter of 30 cm and a height of 30 cm covered with a nylon net containing 20 adult house flies (*Musca domestica*) or female adult mosquitoes (*Culex pipiens*) was hung from the ceiling of an experimental chamber of a volume of 28 m³, and an electrically heated fumigator was placed at the center on the floor of the experimental chamber.

The above prepared solid controlling agent was then heated for 15 minutes on the fumigator and the number of flies or mosquitoes knocked down was observed with the lapse of time. 45 minutes after the initiation of fumigation, the chamber was evacuated, and the insects tested were collected in a glass container for observation and allowed to stand for 24 hours with feeding. The number of flies or mosquitoes killed was then counted and the results obtained are shown in Table 9 below.

TABLE 9

Effects on House Flies or Mosquitoes by Fumigation of Various Active Ingredients at 40 mg/m³ Concentration

Compound	Knocked Down (%) with Lapse of Time (min) 5	10	15	20	25	30	45	Mortality (%)
House Flies								
d-Phenothrin	0	15	65	100	100	100	100	100
Permethrin	0	40	65	100	100	100	100	100
Phenvalerate	0	10	65	90	100	100	100	100
Tetramethrin	0	95	100	100	100	100	100	100
d-Trans Allethrin	0	90	100	100	100	100	100	100
Pyrethrin	0	85	100	100	100	100	100	100
Tetramethrin+ d-Phenothrin (2:1 wt. mixture)	25	100	100	100	100	100	100	100
d-Trans Allethrin+ Permethrin (2:1 wt. mixture)	5	90	100	100	100	100	100	100
Mosquitoes								
d-Phenothrin	0	15	55	95	100	100	100	100
Permethrin	0	5	45	95	100	100	100	100
Phenvalerate	0	0	15	85	100	100	100	100
Tetramethrin	0	50	100	100	100	100	100	100
d-Trans Allethrin	0	90	100	100	100	100	100	100
Pyrethrin	0	55	100	100	100	100	100	100
Tetramethrin+ d-Phenothrin (2:1 wt. mixture)	10	90	100	100	100	100	100	100
d-Trans Allethrin+ Permethrin (2:1 wt. mixture)	10	100	100	100	100	100	100	100

Example 6

The sintered material prepared as described in Reference Example 2 was immersed in an acetone solution of each of the active ingredients shown in Table 10 below at a predetermined concentration which would release, upon fumigation, the active ingredient at a concentration of 40 mg/m³, followed by air-drying to obtain a solid controlling agent in each instance.

The resulting solid controlling agents were then tested according to the procedure as described in Reference Example 4 and the results obtained are shown in Table 10.

TABLE 10

Effects on Cockroaches by Fumigation of Various Active Ingredients at 40 mg/m³ Concentration

Compound	Biological Effects with Lapse of Time (min) 5	10	15	20	25	30	45	60	90	Knocked Down (%) After 24 Hours	Mortality (%) After 72 Hours
Triangular Shelter Method Flushing Out (%)											
d-Phenothrin	0	40	60	90	100	100	100	100	100	100	100
Permethrin	0	20	70	80	100	100	100	100	100	100	100
Phenvalerate	0	0	20	50	90	100	100	100	100	100	100
Tetramethrin+d-Phenothrin (2:1 wt. mixture)	0	20	60	80	90	90	100	100	100	100	100
Tetramethrin+Permethrin (3:1 wt. mixture)	0	20	60	90	100	100	100	100	100	100	100
Tetramethrin+Phenvalerate (1:1 wt. mixture)	0	20	60	80	80	90	100	100	100	100	100
d-Trans Allethrin+d-Phenothrin (1:1 wt. mixture)	0	30	70	90	100	100	100	100	100	100	100
d-Trans Allethrin+Permethrin (2:1 wt. mixture)	0	20	60	80	100	100	100	100	100	100	100
Petri Glass Method Knocked Down (%)											
d-Phenothrin	0	10	50	80	90	100	100	100	100	100	100
Permethrin	0	10	40	80	90	100	100	100	100	100	100
Phenvalerate	0	0	10	60	100	100	100	100	100	100	100
Tetramethrin+d-Phenothrin (2:1 wt. mixture)	0	30	90	100	100	100	100	100	100	100	100
Tetramethrin+Permethrin (3:1 wt. mixture)	0	20	80	100	100	100	100	100	100	100	100
Tetramethrin+Phenvalerate (1:1 wt. mixture)	0	20	70	90	100	100	100	100	100	100	100
d-Trans Allethrin+d-Phenothrin (1:1 wt. mixture)	0	20	70	100	100	100	100	100	100	100	100
d-Trans Allethrin+d-Phenothrin (2:1 wt. mixture)	0	10	60	90	100	100	100	100	100	100	100

Example 7

The sintered material prepared as described in Reference Example 2 was immersed in an ethyl acetate solution of permethrin at the predetermined concentration which would release, upon fumigation, the active ingredient at 40 mg/m³ concentration, followed by air-drying to obtain a solid controlling agent containing permethrin.

An electrically heated fumigator and 9 Petri dishes (14 cm diameter×7 cm height) each containing 10 cockroaches (*Blattella germanica*) were arranged on the floor of an experimental chamber of a volume of 28 m³ (2.65 cm width×4.3 cm depth×2.54 cm height) as shown in Figure 2. More specifically, 3 Petri dishes each containing 10 cockroaches (2, 3 and 4); 1 Petri dish containing a filter paper at the bottom thereof and containing 10 cockroaches thereon (5); 2 Petri dishes each containing 10 cockroaches and covered with a filter paper having a slit of 3 cm×10 cm at the top of Petri dishes while leaving, about 1/5 of the area uncovered and open to imitate small opening conditions such as gaps or spaces in drawer openings (6 and 7); 1 Petri dish containing (i) a filter paper at the bottom thereof, (ii) a triangular shelter (3 cm×15 cm) of plywood board at the center of the dish and (iii) 10 cockroaches in the shelter (8); and 1 Petri dish containing a triangular shelter (3 cm×15 cm) of plywood board at the center of the dish and 10 cockroaches in the shelter (9), were arranged at the distances shown in Figure 2. The electrically heated fumigator (1) was placed at the center of the floor of the experimental chamber.

The above prepared solid controlling agent containing permethrin was heated on the fumigator for 15 minutes and the number of cockroaches flushed out and the number of cockroaches knocked down were counted with the lapse of time. 90 minutes after the fumigation, the chamber was evacuated, and each group of cockroaches tested were collected in each of containers for observation and allowed to stand for 72 hours with feeding. The number of cockroaches knocked down was counted 24 hours after the fumigation and the number of cockroaches killed was counted 72 hours after fumigation. The results obtained are shown in Table 11 below.

TABLE 11

Effects on Cockroaches by Fumigation of Permethrin at 40 mg/m³ Concentration under Various Conditions

Test Conditions	Observation Items	Dish No.	Biological Effects with Lapse of Time (min) 5	10	15	20	25	35	45	60	90	Knocked Down (%) After 24 hrs.	Mortality (%) After 72 hrs.
Petri Dish No. 9	% FO	9	0	50	80	90	100	100	100	100	100		
	% KD*	9	0	20	50	90	100	100	100	100	100	100	100
Petri Dish No. 8	% FO	8	0	20	70	80	90	100	100	100	100		
	% KD*	8	0	0	0	10	20	80	100	100	100	100	100
Petri Dishes Nos. 2, 3 and 4	% KD	2	0	10	60	70	90	100	100	100	100	100	100
		3	0	10	40	90	100	100	100	100	100	100	100
		4	0	20	70	80	100	100	100	100	100	100	100
Petri Dish No. 5	% KD	5	0	0	10	70	100	100	100	100	100	100	100
Petri Dishes Nos. 6 and 7	% KD	6	0	0	20	40	80	100	100	100	100	100	100
		7	0	10	50	50	80	100	100	100	100	100	100

Note

% FO=Percent Flushed Out

% KD= Percent Knocked Down

% KD*= Percent Knocked Down in Petri Dishes after flushing out from triangular shelter.

Example 8

4.8 g of gypsum as a mineral powder and as an active ingredient 0.8 g Tetramethrin and 0.4 g Phenothrin were mixed and kneaded together with water of an amount necessary to harden the gypsum. The kneaded product was molded at room temperature into a perforated cylindrical column with a diameter of 33.4 mm, a height of 13 mm and 48 pores having a diameter of 3 mm. The column was then allowed to stand to obtain a perforated solid controlling agent. The thus obtained solid controlling agent was heated on a fumigator by passing an electric current for 15 minutes in a kitchen with a volume of 18 m^3 in a reinforced ferroconcrete honse thereby to vaporize the active ingredient in the controlling agent. When the kitchen was kept closed for 150 minutes, it was found that 356 adult German cockroaches (*Blattella germanica*) and 5 adult brown cockroaches (*Periplaneta picea* Shiraki) were flushed out and knocked down.

None of the cockroaches were alive after 48 hours. Thereafter, the controlling effect was examined over a 70-day period of time in the same manner as that described in Example 1, but no cockroaches were found at all in the kitchen.

WHAT WE CLAIM IS:—

1. A controlling agent for controlling injurious insects which comprises, as an active ingredient, an insecticidally effective amount of at least one insecticidally active compound retained in a porous solid mineral material, the controlling agent having a ratio of the total surface area to the volume of 5:1 cm^{-1} or higher.

2. A controlling agent as claimed in Claim 1, wherein said porous solid mineral material is cement, gypsum, diatomaceous earth, alumina, perlite, calcium silicate, titanium oxide, calcium carbonate or barium sulfate.

3. A controlling agent as claimed in Claim 1, or Claim 2, wherein the controlling agent contains 3 to 30% by weight of at least one insecticidally active compound.

4. A controlling agent as claimed in any one of the preceding Claims, wherein said controlling agent comprises the product obtained by impregnating a molded porous solid mineral material with at least one insecticidally active compound, or mixing and kneading a powder of a porous solid mineral material with at least one insecticidally active compound and then molding the resulting mixture.

5. A controlling agent as claimed in any one of the preceding Claims, substantially as hereinbefore described with reference to the Examples.

6. A method of controlling injurious insects which comprises heating a controlling agent as claimed in any one of the preceding Claims, utilizing a rising heated air current capable of heating the controlling agent at 200 to 430°C to thereby vaporize the active ingredient in the controlling agent within a short period of time and causing the vaporized active ingredient to come into contact with injurious insects.

7. A method as claimed in Claim 6, of controlling injurious insects substantially as hereinbefore described with reference to the accompanying drawings.

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1601095 COMPLETE SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
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FIG.1.

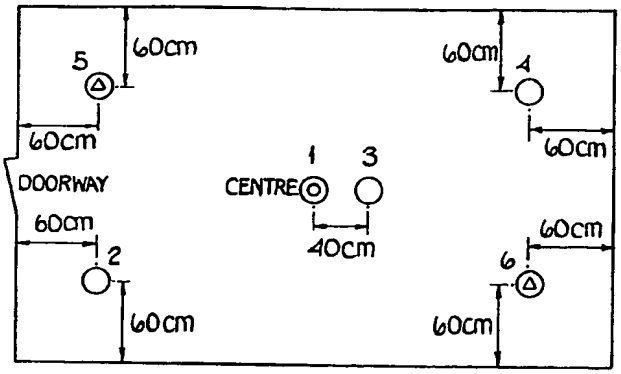
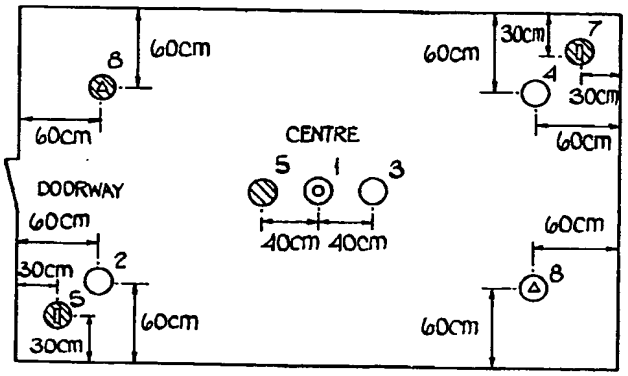


FIG.2.



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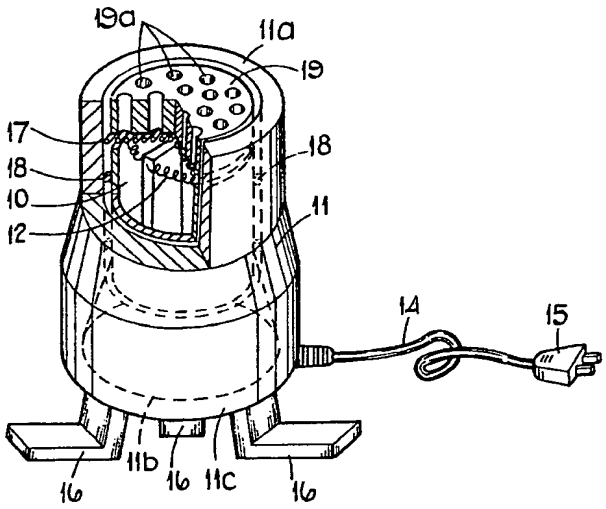
Sheet 2

FIG.3.



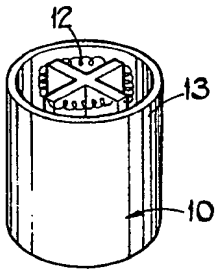


FIG.4.

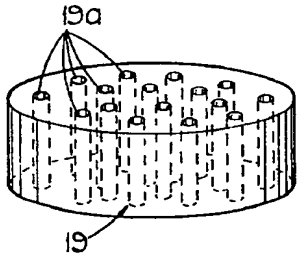


FIG.5.